GAS CHROMATOGRAPHIC DETERMINATION OF HIGHER BOILING HOMOLOGUES IN ASTM D2233 TYPE D AND TYPE A (1)

1. SCOPE

1.1 This is a rapid empirical procedure to be used to determine the level of higher boiling homologues in ASTM D2233 Type D and Type A. Higher boiling homologues are defined in paragraph 2.2. This procedure is not intended for the absolute analysis of polychlorinated biphenyl products or mixtures.

2. SUMMARY OF METHOD

2.1 The sample is injected into a support-coated open tubular gas chromatography column. The components are separated as they pass through the column with helium carrier gas and their presence in the effluent is measured by a flame ionization detector and recorded on a chromatogram. The method is made quantitative by internal normalization comparing the area of the higher boiling homologue peaks to the total area of all the peaks in the chromatogram.

Note 1 - Reference should be made to ASTM Method E260, General Gas Chromatography Procedures and ASTM Method E355, Gas Chromatography Terms and Relationships (2).

2.2 This method arbitrarily splits up the chromatogram into two regions. The major region represents mostly mono, di, tri and tetra-chlorobiphenyls. The lesser region represents the higher boiling homologues and is mostly penta and hexa-chlorobiphenyls. However, there is some overlap of the tetra and penta-chlorobiphenyls between the two regions. Some of the important peaks in the major region contain both tetra and penta-chlorobiphenyls.

The only way to obtain a closer approximation to true composition of these samples is to use a longer column with a gas chromatography/mass spectrometry combination to correct for the composition of these overlap peaks. Area correction factors must also be used. However, GC/MS instrumentation is not available in many laboratories and is too cumbersome and costly for routine analysis. Therefore, this empirical short method has been adopted.

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(1) This method is under the jurisdiction of ASTM Committee D-27 on Electrical Insulating Liquids and Gases.

(2) Annual Book of ASTM Standards, Part 30.

3. SIGNIFICANCE

3.1 Present knowledge indicates that higher boiling homologs of chlorinated biphenyls are less degradable than the lower boiling homologs, if present in the environment.

3.2 Because of the disposal method of certain types of capacitors containing these askarels, it is important to limit the higher boiling homolog content.

3.3 This method is used as a process control and acceptance test for ASTM D2233 Type D.

4. APPARATUS

4.1 Chromatograph - Any gas chromatograph with flame ionization detector and capillary column inlet splitter system.

4.2 Recorder - 0 to 1 or 10 mV range with full-scale response time of 1 sec. and chart speed of approximately 1/2 inch/min.

4.3 Column - Fifty foot by 0.02 inch I.D. support-coated open tubular (S.C.O.T.) capillary coated with FFAP available from Perkin-Elmer Corporation as Part No. 008-0804.

4.4 Integrator - Disc chart integrator or electronic digital integrator to measure the peak areas. If an electronic integrator is used, it should be checked initially against a Disc chart integrator to determine that the electronic integrator operating parameters have been set properly for correctly measuring the late eluting small peaks.

5. INSTRUMENT PARAMETERS

5.1 Column - 50' x 0.02" I.D. Support-coated open tubular capillary coated with FFAP (Perkin-Elmer Part No. 008-0804).

5.2 Temperatures -

Column: 220° C (isothermal)
Sample Inlet System: 320°C
Detector: 300°C

5.3 Gas Flow Rates -

Column: 8 ml/min. (7 PSIG) helium
Inlet Splitter: 210 ml/min, helium
Auxiliary or Make-Up: 50 ml/min. helium
Hydrogen: Note 3
Air: Note 3

3.2 Because of the disposal method of certain types of capacitors containing these askarels, it is important to limit the higher boiling homolog content.

Note 3 - Adjust air-hydrogen ratio to give maximum detector sensitivity. See the Instrument Instruction Manual.

5.4 Sample Size - 0.005 ml split 1 to 25.

6. CALIBRATION

6.1 The method of calculation is peak area normalization. The lack of pure knowns prevents the accurate determination of response factors (area correction factors) for the individual components. Therefore, the results are reported as area percent of higher boiling homologues.

7. PROCEDURE

7.1 Adjust the chromatograph to the above conditions.

7.2 Inject 5 µℓ of the neat sample and allow the chromatogram to proceed at attentuation settings which will keep all the peaks on the scale if the Disc chart integrator is being used.

7.3 Final check-out of the total chromatographic system for this analysis can best be done using the reference samples of Aroclor 1016 and Aroclor 1242 referred to in the Precision Section.

Portions of these two reference samples are available from Dr. E. M. Emery, Monsanto Company, Mail Zone T3E, 800 No. Lindbergh Blvd., St. Louis, Missouri 63166.

8. CALCULATION

8.1 Divide the chromatogram into two regions as shown on the accompanying chromatograms.

8.2 Measure the total area of the peaks in each region of the chromatogram.

8.3 Calculate the result as follows:

$$\text{Area \% Higher Boiling Homologues} = \frac{\text{Area of Higher Boiling Homologues}}{\text{Total Area of All Peaks}} \times 100$$

9. PRECISION

9.1 Reference samples of Aroclor 1016 (Drum 2) and Aroclor 1242 (Lot KK 491) were analyzed in duplicate on two different instruments using both the Disc chart integrator and an electronic integrator. An Infotronics Model CRS-100 integrator was used on a Perkin-Elmer Model 800 chromatograph and a Hewlett-Packard Model 3370A integrator was used on a Hewlett-Packard Model 7624A chromatograph. The same column was used in both instruments.

9.2 Results are given below in Area % Higher Boiling Homologues:

	Method of Integration		
Chromatograph	Disc Chart	Infotronics CRS-100	Hewlett-Packard 3370A
Aroclor 1016 (Drum 2) :			
Perkin-Elmer 800	0.30, 0.27	0.23, 0.21	0.27, 0.28
Hewlett-Packard 7624A	0.30, 0.30	-	
Aroclor 1242 (Lot KK 491):			
Perkin-Elmer 800	5.88, 5.78	6.22, 5.94	6.63, 6.50
Hewlett-Packard 7624A	6.14, 6.32	-	

9.3 The above two reference samples were each analyzed five times in another laboratory using a Varian-Aerograph Model 144410-00 gas chromatograph with an Infotronics Model CRS-11-HS electronic integrator. The 95% confidence limits of the mean were calculated as follows:

$$95\% \text{ confidence limits of mean} = \pm \frac{tS}{\sqrt{5}}$$

where

$t = 2.78$ for five measurements

S = estimated standard deviation

$= (0.43)(\text{Range of five measurements})$

Results:

	Aroclor 1016 (Lot KK 491)	Aroclor 1242 (Drum 2)
Mean	0.35	6.80
S	0.0043	0.129
95% Confidence Limits	0.0053	0.124

10. SENSITIVITY AND DETECTION LIMIT

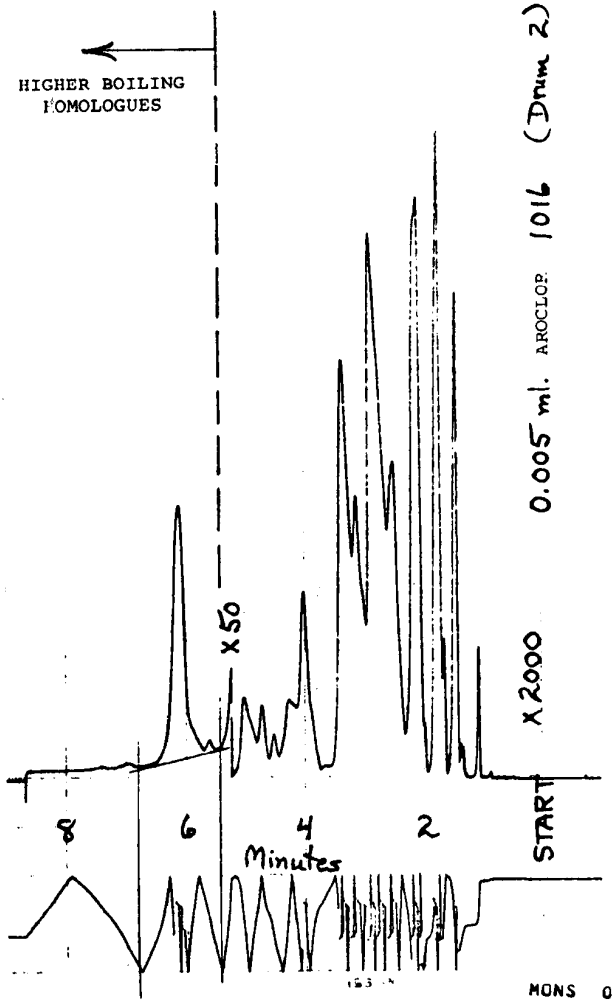
10.1 These values were determined according to ASTM Method E260 for biphenyl on the Perkin-Elmer Model 800 Gas Chromatograph.

Results:

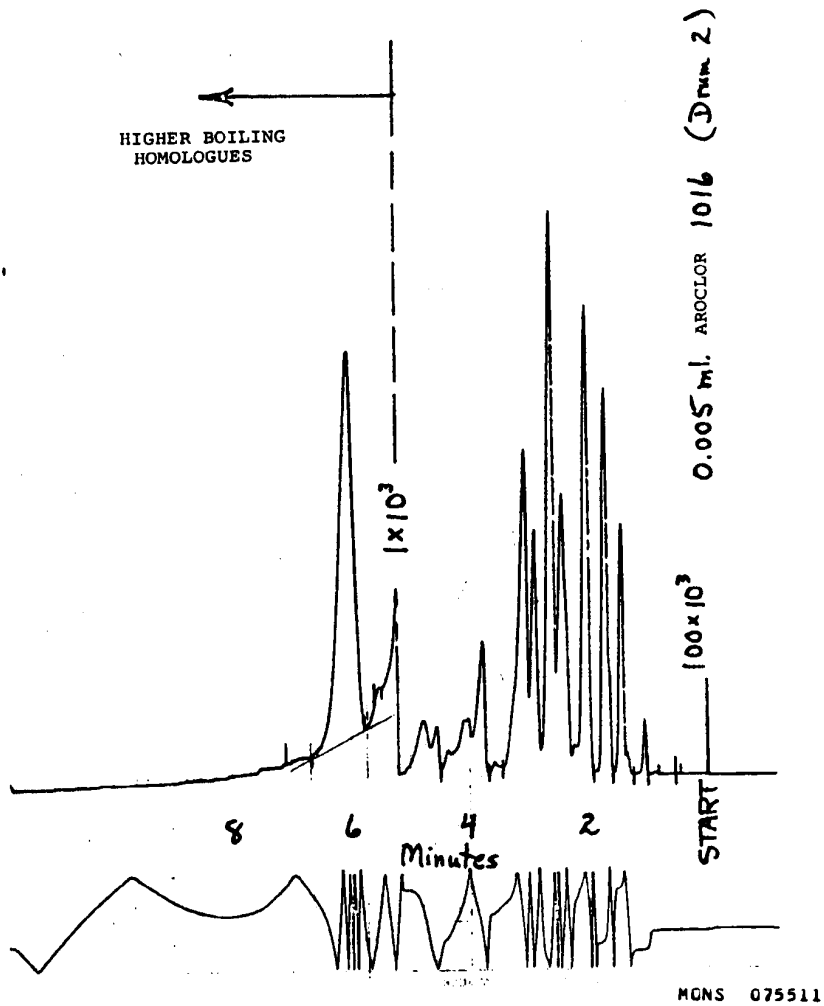
Sensitivity = $S' = 2.37 \times 10^{4}$ mV·min/millimole

Detection Limit = $Q_{\ell} = 2.82 \times 10^{-8}$ millimoles/ml

Perkin-Elmer 800



Hewlett-Packard 7624A



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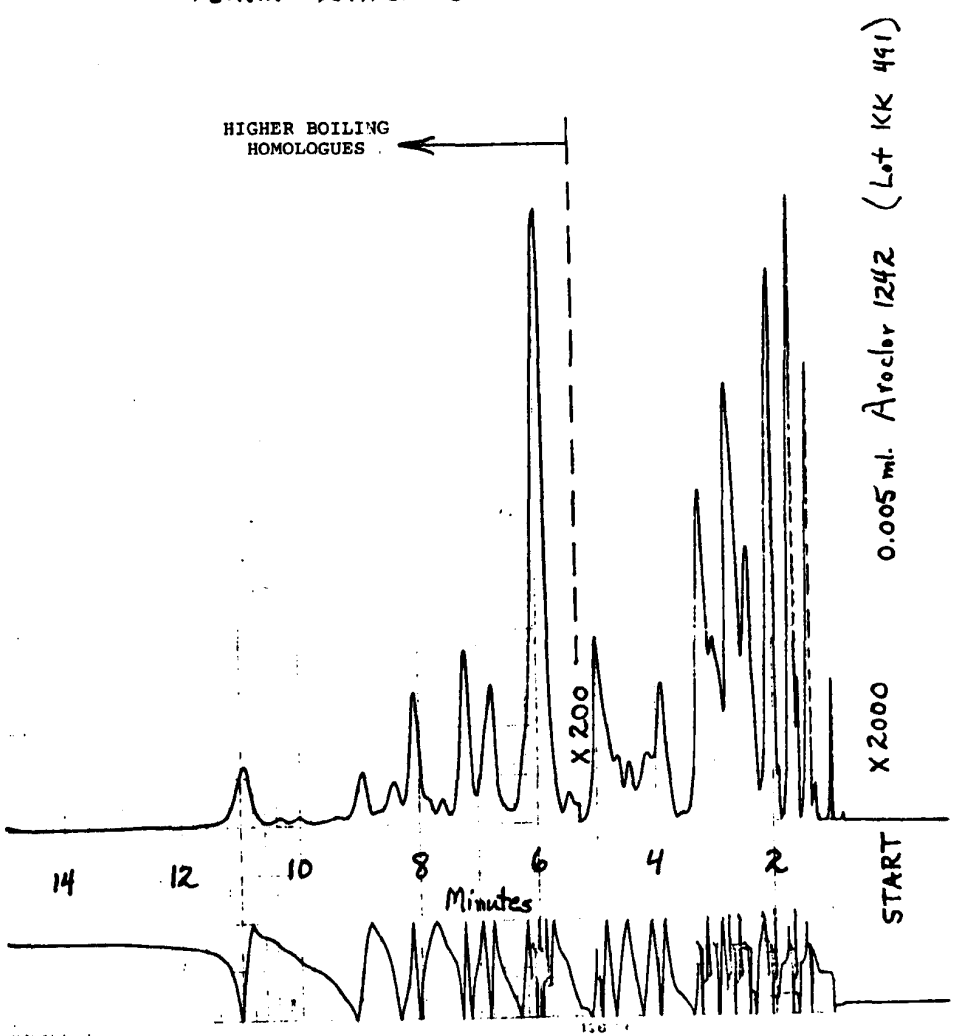
Perkin - Elmer 800
HIGHER BOILING HOMOLOGUES
0.005 ml. Aroclor 1242 (Lot KK 491)
X 2000
X 200
START
14
12
10
8
6
4
2
Minutes

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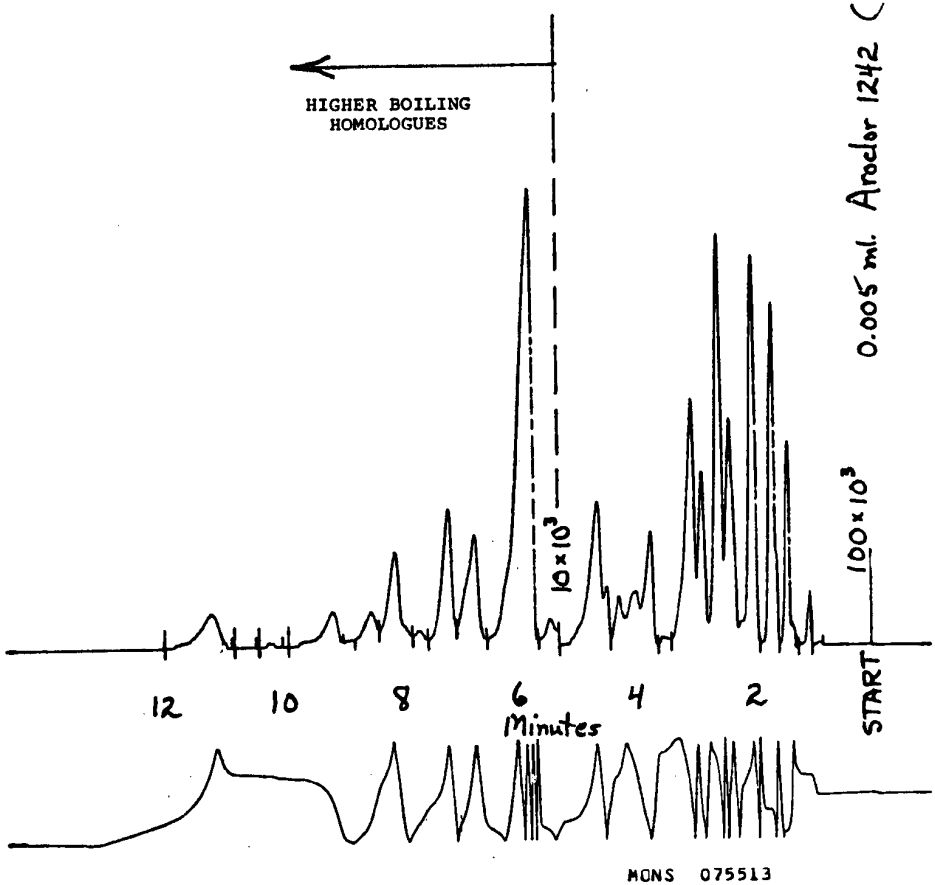
Hewlett-Packard 7624A



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